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(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 764 741 A2

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
26.03.1997 Bulletin 1997/13

(51) Int Cl.[6]: **D21H 27/16**, D21H 17/34

(21) Application number: **96306636.0**

(22) Date of filing: **12.09.1996**

(84) Designated Contracting States:
AT BE DE ES FI FR GB IT SE

(30) Priority: **21.09.1995 JP 266197/95**

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(54) **Dust-free paper**

(57) A composition for dust-free paper comprising a polymer composition which contains polymeric substance having glass transition temperature (Tg) in -20°C ~ 70°C range and a polymeric substance having glass transition temperature (Tg) in -65°C ~ 10°C range, where the difference of the glass transition temperatures of these two types of polymeric substances is 30°C or above and the average glass transition temperature (tg) is in -30°C ~20°C range.

EP 0 764 741 A2

Printed by Jouve, 75001 PARIS (FR)

Description

This invention relates to dust-free paper, and more particularly this invention intends to provide dust-free paper to be used in clean room, etc. which excels in stiffness and blocking resistance, prepared by including in the paper a polymer composition containing two different polymeric substances having specific and different glass transition temperatures (Tg).

In high tech industries such as semiconductor producing industry, pharmaceutical industry, food production, and precision machine industry, extremely clean environment is required for the clean room where various works are performed because minute dust or dirt may cause failure of equipment or form defective products.

Because recording paper used in various equipments or writing paper being used in the clean room, etc. is one of the sources of dusts and dirt, synthetic resin paper made of polyethylene or polystyrene have been developed. However, they are not used extensively because such synthetic resin paper is more expensive, has poorer printing adaptability and heat resistance compared to the paper made of cellulose pulp.

Papers made of cellulose pulp and contained polymeric substance have been used in the past to improve heat resistance, solvent resistance, and water resistance, and they are used widely also to prevent formation of dust.

For example, the invention disclosed in Japanese Patent Publication (Kokai) 146099/85 relates to dust-free paper which was impregnated or coated with a polymeric substance having a minimum film-forming temperature of no higher than 10°C. The polymeric substances that are used in that invention are emulsion or latex formed from polyacrylate, polyvinyl acetate, and polyvinylchloride type copolymers. Specific examples are the emulsion of polyvinyl acetate, polyacrylate, and polyvinyl acetate/ethylene/acrylate copolymer.

Japanese Patent Publication (Kokai) 105199/88 discloses a preparation method of dust-free paper, by impregnating or coating a hollow pigment, together with synthetic resins having a glass transition temperature of no higher than 0°C, such as polyacrylate, polyvinyl acetates or polyethylene or latex, in paper.

And, Japanese Patent Publication (Kokai) 167996/75 discloses a dust-free paper prepared by adding a polymeric substance having glass transition temperature of no higher than 0°C in paper. Examples of the polymeric substance are emulsion of acrylic ternary copolymer, acrylate ester polymer, and vinyl acetate/acrylic acid copolymer, which is impregnated in paper by dipping. It demonstrates that the amount of dust generated from the paper decreases as the glass transition temperature decreases, and that the amount of dust formed will be extremely small particularly when the Tg is -50°C.

However, the real problem is as follows. Thus, although the amount of dust generated will be extremely small when a polymeric substance having low glass transition temperature, and particularly when the glass transition temperature in -40°C ~ -50°C is included in the paper made of cellulose pulp, such paper tends to show excessively high blocking property and lower stiffness. And, on the other hand, although the paper may show stiffness when the glass transition temperature is in 0°C ~ -20°C range, there is no reduction in the amount of dust formed. Therefore, there is a demand for a dust-free paper that is equipped with both characteristics, i.e. a dust-free paper with stiffness and blocking resistance.

This invention provides a composition for dust-free paper comprising a polymer composition which contains a polymeric substance having a glass transition temperature (Tg) in -20°C ~ 70°C range and a polymeric substance having glass transition temperature (Tg) in -65°C ~ 10°C range, where the difference of the glass transition temperatures of the polymeric substances is 30°C or above, preferably 50°C or above, and most desirably 70°C or above, and the average glass transition temperature (tg) is in -30°C ~ 20°C range, preferably in -20°C ~ -10°C range.

In this invention, the mixing ratio of the polymeric substance having glass transition temperature (Tg) in -20°C ~ 70°C range and the polymeric substance having a glass transition temperature (Tg) in -65°C ~ 10°C range is preferably in 20:80 ~ 80:20 range, more preferably in 70:30 ~ 30:70 range.

This invention further provides a dust-free paper on which the above-said composition for dust-free paper was carried.

The composition for dust-free paper of this invention is mixed with a dust free at 3 weight % ~ 100 weight %, preferably 5 weight % ~ 50weight %, by the weight of the paper.

Dust-free paper with excellent paper stiffness and blocking resistance can be obtained by using the composition for dust-free paper composition of this invention.

Any of the natural polymers and synthetic polymers can be used as the polymeric substance in this invention. Example of natural polymer is natural rubber, and examples of synthetic polymeric substance are synthetic rubber; polymers and copolymers obtained by polymerizing ethylenic unsaturated monomers such as ethylene, propylene, vinyl chloride, vinyl acetate, styrene, acrylonitrile, methacrylonitrile, acrylates, methacrylate, acrylic acid, or methacrylic acid; and diene monomers such as butadiene or isoprene, etc.. when polymerizing or copolymerizing such monomers, polyethylenically unsaturate monomers such as ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, divinylbenzene, trimethylol propane trimethacrylate and allyl methacrylate can be incorporated.

In this invention, the polymeric substance having glass transition temperature (Tg) in -20°C ~ 70°C range is a hard

component and the polymeric substance having glass transition temperature (Tg) in -65°.C ~ 10° C range is a soft component. Preferred range of the Tg of the hard component is -10°C ~ 50°C, and 0°C ~ 40°C range is even mor desirable. And, preferred range of the Tg of soft component is -55°C ~ -10°C, and -55 °C ~ -35°C range is even more desirable. Glass transition temperature of the hard component is higher than the glass transition temperatures of th soft component by more than 30°C, preferably more than 50°C. And a differenc of more than 70°C is even more desirable.

In this invention, a plurality of polymers can be used for the hard component and the soft component, as long as each of them meets the above-said requirements.

In the composition of this invention, the average glass transition temperature (tg) of the hard component and soft component is in -30°C ~ 20 °C range, preferably in -20°C ~ -10°C range. If the average glass transition temperature is lower, the paper will not be as stiff and the blocking property will be poor. On the other hand, if the average glass transition temperature is higher, it generates more dust, which is not desirable.

Glass transition temperature of the polymers can be calculated by the following Fox's equation [Bulletin of American Physical Society, 13, p123(1956)].

$$1/Tg = W_1/Tg(1) + W_2/Tg(2)$$

Here, W_1 and W_2 are weight fraction of the component 1 and component 2, and Tg(1) and Tg(2) represent, respectively, the glass transition temperature (unit : absolute temperature) of the homopolymer of component 1 and homopolymer of component 2.

And, the average glass transition temperature (tg) in this invention can be determined from the above-described Fox's equation, using the glass transition temperature (Tg) of the polymer or homopolymer.

$$1/tg = W_1/Tg(1) + W_2/Tg(2)$$

Here, W_1, and W_2 are weight fractions of homopolymer or copolymer components 1 and 2, respectively, and Tg (1) and Tg(2) represent the glass transition temperature (unit: absolute temperature) of the polymer component 1 and polymer component 2.

Although many methods and known as the methods for determination of the real glass transition temperature of the obtained polymer, the differential scanning calorimetry (DSC) is a convenient and accurate method to use.

Average glass transition temperature may be determined by analyzing for monomer and calculating using the Fox's equation.

Table 1 shows the glass transition temperatures of typical polymers used in the invention.

Table 1

Polymer	Tg (°C)
Polymethyl acrylate	13
Polyethyl acrylate	-17
Poly(n-butyl acrylate)	-45
Poly(s-butyl acrylate)	-18
Poly(2-ethylhexyl acrylate)	-65
Polyhydroxyethyl acrylate	-15
Polyacrylic acid	110
Polymethacrylic acid	155
Polymethyl methacrylate	83
Polyethyl methacrylate	55
Poly(n-butyl methacrylate)	20
Poly(i-butyl methacrylate)	20
Polyhydroxyethyl methacrylate	55
Polyhydroxypropyl methacrylate	73
Polyglycidylmethyl methacrylate	46
Polyacrylamide	165
Polyacryl nitrile	140

Table 1 (continued)

Polymer	Tg (°C)
Polyvinyl chloride	80
Polyvinyl acetate	33
Polybutadiene	-83
Polystyrene	83
Polyitaconic acid	165

Mixing ratio of the hard polymeric substance and soft polymeric substance may be changed preferably in 20:80 ~ 80:20 range, more preferably in 70:30 ~ 30:70 range, assuming that the average glass transition temperature is in -30°C ~ 20°C range.

Soft polymer'component and hard polymer component can be prepared by any of the known methods.

These polymer components are used as an aqueous solution, solvent solution, or as an emulsion, and emulsion form is used preferably. For example, the method of preparing first the emulsions of each polymeric substances and then mixing the polymer emulsions together to form the film-forming composition for dust-free paper of this invention is the most simple and convenient method.

And, core/shell polymer, i.e. a polymer having an inner core phase of a polymeric substance and an outer shell phase of polymeric substance, can be used also. Although this core/shell polymer can be prepared by a known production process, it is particularly desirable to provide such core/shell polymer as an emulsion produced by multiple stage emulsion polymerization process. For example, it is obtained by forming first the core phase using the above-said ethylenic unsaturated monomer, and subsequently forming the outer shell phase using another ethylenic unsaturated monomer. Although either the core phase or shell phase may be made of a hard component, it is generally desirable to use a hard component as the core phase and soft component as the shell phase.

The internally plasticized polymer latex particles in which a hard polymer is copolymerized to the soft polymer latex particle may be used also. Such internally plasticized polymer latex particles can be prepared by polymerizing the first charge of ethylenically unsaturated monomer that contains a relatively hydrophilic monomer in emulsion under ordinary condition of emulsion polymerization, and subsequently polymerizing the second charge of ethylenically unsaturated monomer which is the precursor of a polymer which is harder and more hydrophobic than the first charge polymer.

The present'invention, as its one embodiment, provides a method for producing dust-free paper wherein a polymer composition is prepared by mixing a polymer substance having a glass transition temperature (Tg) in a range of -20°C to 70°C and another polymer substance having a glass transition temperature (Tg) in a range of -65°C to 10°C, a difference between their glass transition temperatures being 30°C or above, and an average glass transition temperature (tg) being in a range of -30°C to 20°C, at a ratio of 95:5 to 5:95, and the produced composition for dust-free composition is carried on paper.

There is no particular restriction about the type of paper that can be used in this invention. For example, pulp paper made of wood material or paper made mainly of wood pulp, paper made of regenerated fiber such as rayon, semisynthetic paper such as acetate paper, synthetic paper made of polyvinyl alcohol, polyamide, polyacrylonitrile or polyester, and synthetic pulps made of polyethylene or polypropylene can be used. These paper stock may be added ahead of time with various types of additives such as sizing agent, pigment, drying enhancement agent, wet strength-enhancement agent and so on. These additives may be added at the same time when the composition for dust-free paper of this invention is carried on paper.

In case of preparing the dust-free paper using the film-forming composition for dust-free paper of this invention, the amount of the composition for dust-free paper to be mixed is normally 3 weight % ~ 100 weight %, preferably 5 weight % ~ 50 weight %, and even more desirably 10 ~ 30 weight %, by the weight of paper. And, any known ordinary agent to enhance the dust-preventing effect, such as electrically conductive salts, wax, etc. may be used, and it may be applied after a proper dilution.

Any known method may be used to carry the composition for dust-free paper of this invention in or on paper. For example, it may be carried by impregnation method, size press method, spray method, or coating method in an impregnator or on a paper making machine, or it may be carried on paper after the paper was made.

This invention is explained by way of the following examples which, however, and not intended to limit the scope of this invention.

Examples

Example 1 Preparation of polymer composition

1-1) Nonionic surfactant 7g and deionized water 340g were charged in a 3 liter flask equipped with an agitator, a thermometer, a reflex condensor and a N2 gas inlet port, and nitrogen gas was sparged. Then, after adding a pre-emulsion 230 g made of deionized water 550g, nonionic surfactant 70g, itaconic acid 25g, ethyl acrylate 591g, and methyl methacrylate 401g in the flask, deionized water 17g containing ammonium persulfate 0.20g as the initiator, deionized water 17g containing sodium hydrosulfite 0.16g, and deionized water 10g containing ferrous sulfate 0.02g were added, to initiate the polymerization reaction. After polymerization reaction started and the temperature reached about 50°C, the remaining pre-emulsion, deionized water 40g containing ammonium persulfate 1.3g, and deionized water 40g containing sodium bisulfite 2.0g were added over a period of 3 hours. During the course of addition, temperature was kept at 60°C. After the reaction mixture was cooled down to room temperature, it was neutralized with a neutralizing agent and filtered through a 100 mesh metal filter, to obtain an emulsion (Emulsion 1).

When the glass transition temperature of the thus-obtained emulsion was measured by the following method, it was 20°C.

Preparation of sample

Several drops of the thus-obtained emulsion were injected into a sample holder of DSC analyzer, and dried at 60°C for 1 day, so that the solid content would be 10 ~ 40mg. In this case, in order to maintain the same thermal history, temperature of the acquired sample was raised to 160°C and then allowed to cool down naturally to room temperature, before running the DSC analysis.

DSC analysis

Using a Schimatzu DSC 50, the sample was cooled to -100°C by liquid nitrogen. Temperature was raised at a rate of 10°C/minute, to determine the heat flow - temperature curve. In the analysis, Tg is determined as a temperature at the midpoint of heat capacity change due to glass transition.

1-2) Procedure of Example 1-1) was repeated, except setting the composition of the pre-emulsion to have deionized water 550g, nonionic surfactant 70g, itaconic acid 25g, butyl acrylate 944g, and ethyl acrylate 48g.

The thus-acquired emulsion 2 gave Tg = -50°C

1-3) Emulsion 1 and Emulsion 2 were blended at the following ratios, to obtain Emulsion 3, Emulsion 4, and Emulsion 5.

Emulsion 3 (tg = -16°C)	Emulsion 1/Emulsion 2 = 550/450
Emulsion 4 (tg = -11°C)	Emulsion 1/Emulsion 2 = 620/380
Emulsion 5 (tg = - 5°C)	Emulsion 1/Emulsion 2 = 700/300

Example 2 Preparation of polymer composition

Nonionic surfactant 7g and deionized water 320g were charged in a 3 liter flask equipped with an agitator, a thermometer, a reflux condensor and a N_2 gas inlet port, and nitrogen gas was sparged. Then, after adding the pre-emulsion 230g made of deionized water 304g, nonionic surfactant 39g, itaconic acid 14g, ethyl acrylate 325g, and methyl methacrylate 220g, deionized water 17g containing ammonium persulfate 0.20g as the initiator, deionized water 17g containing sodium hydrosulfite 0.16g,, and deionized water 10g containing ferrous sulfate 0.02g were added, to initiate the polymerization reaction. After polymerization reaction started and the temperature reached about 50°C, the remaining pre-emulsion, deionized water 28g containing ammonium persulfate 0.9g, and deionized water 28g containing sodium bisulfite 1.3g were added over a period of 2 hours. During addition, temperature was kept at 60°C. After the addition, the reaction mixture was kept for 30 minutes, and then a pre-emulsion containing deionized water 245g, nonionic surfactant 32g, itaconic acid 12g, butyl acrylate 425g, and ethyl acrylate 22g, deionized water 14g containing ammonium persulfate 0.5g, and deionized water 14g containing sodium bisulfite 0.7g were added over a period of 1 hour. During the course of addition, temperature was kept at 60°C.

After cooling down to room temperature, reaction mixture was neutralized with a neutralizing agent, and filtered through a 100 mesh metal filter, to obtain an emulsion (Emulsion 6: Tg of the core = 20°C, Tg of the shell = -50 °C).

Example 3

The procedure of Example 1-1) was repeated, except changing the composition of the pre-emulsion to deionized water = 550g, nonionic surfactant = 70g, itaconic acid = 25g, ethyl acrylate = 887g, and methyl methacrylate =106g.
Emulsion 7 (Tg = -10°C) was thus obtained.
Emulsion 7 and emulsion 2 were blended at a ratio of Emulsion 7/ Emulsion 2 = 700/300, to obtain Emulsion 8.

Example 4

The procedure of Example 1-1 was repeated, except changing the composition of pre-emulsion to deionized water = 550g, nonionic surfactant =70g, ethyl acrylate = 152.6g, methyl methacrylate = 152.6g, butyl acrylate = 681.4g, and methacrylic acid =30.4 g.
Emulsion 9 (Tg = -30°C) was thus obtained.
Emulsion 7 and Emulsion 9 were blended at a ratio of Emulsion 7/Emulsion 9 = 700/300, to obtain the Emulsion 10.
A list of these samples are shown in the following Table 2.

Table 2[1]

Sample	Tg (°C)		Tg(°C)difference	Average tg(°C)
(Comparative) Emulsion 1	Emulsion 1	20	-	-
(Comparative) Emulsion 2	Emulsion 2	-50	-	-
(Present invention) Emulsion 3	Emulsion 1	20		
	Emulsion 2	-50	70	-16
(Present invention) Emulsion 4	Emulsion 1	20		
	Emulsion 2	-50	70	-11
(Present invention) Emulsion 5	Emulsion 1	20		
	Emulsion 2	-50	70	- 5
(Present invention) Emulsion 6	Corepolymer	20		
	Shellpolymer	-50	70	-16
(Comparative) Emulsion 7	Emulsion 7	-10	-	-
(Present invention) Emulsion 8	Emulsion 7	-10		
	Emulsion 2	-50	40	-23
(Comparative) Emulsion 9	Emulsion 9	-30	-	-
(Comparative) Emulsion 10	Emulsion 7	-10		
	Emulsion 9	-30	20	-16

Example 5 Preparation of impregnated paper

A paper stock cut into A-4 size was dipped in a bath where the concentration of emulsion was 13% for impregnation,

and then the excess emulsion was removed by passing the wet paper through a set of two rubber rolls, so that the content of acrylic resins (based on the weight of the original paper stock) would be 15 weight %. subsequently, it was dried for 3 minutes on a chrome plated steam drum whose surface temperature was set at 90°C.

Testing method of determing the degree of dust formation

Prior to the test, dust on the surface was brushed off. Two pieces of A-5 size paper were superimposed (front surface against the rear surface) in the tester and they were rubbed against each other at a rate of once per 2 seconds for 1 minute.

Tester : Total number (per cubic feet) of particles having a size 0.3μm or above was counted with Dustcounter of a light-scattering particle counter (manufactured by Lyon Co.), to evaluate the cleanliness. Lower value showed a better cleanliness.

Paper stiffness test

Paper stiffness was tested by the procedure described in TAPPI (1991 Edition, T451 cm-84). Evaluation was based on the following grading standard.

5 : Paper is stiff
4 : Paper has some stiffness
3 : Medium degree of paper stiffness
2 : Paper has almost no stiffness
1 : Paper has absolutely no stiffness

Blocking resistance

Blocking resistance was measured by the procedure described in TAPPI (1991 Edition, T521 cm-85). Evaluation was based on the following grading standard.

5 : Absolutely no blocking
4 : No blocking
3 : Blocking was ordinary
2 : Some blocking
1 : Very strong blocking

Amount of dust formed, and results of evaluation of stiffness and blocking resistance of paper are shown in Table 3.

Table 3

Sample	Amount of Dust	Stiffness	Blocking Resistance
Emulsion 1	>500	5	5
Emulsion 2	0	1	1
Emulsion 3	4	5	5
Emulsion 4	6	5	5
Emulsion 5	7	5	5
Emulsion 6	4	5	5
Emulsion 7	43	5	5
Emulsion 8	13	4	4
Emulsion 9	18	2	2
Emulsion 10	30	4	4

The dust-free paper of this invention forms very little amount of dust, and excels in paper stiffness and blocking resistance. Therefore, the dust-free paper of this invention can be used in broad area such as the recording paper for various types of equipments, writing paper, or printed matters which are to be used in a clean room.

Claims

1. A composition for dust-free paper comprising a polymer composition which contains a polymer substance having a glass transition temperature (Tg) in a range of -20°C to 70°C and a polymer substance having a glass transition temperature (Tg) in a range of -65°C to 10°C at a ratio of 95:5 to 5:95, a difference between their glass transition temperatures being 30°C or above, and an average glass transition temperature (tg) being in a range of -30°C to 20°C.

2. A composition for dust-free paper according to Claim 1, wherein a mixing ratio of the polymer substance having a glass transition temperature (Tg) in a range of -20°C to 70°C and the polymer substance having a glass transition temperature (Tg) in a range of -65°C to 10°C is in a range of 20:80 to 80:20.

3. A composition for dust-free paper according to Claim 1, wherein a mixing ratio of the polymer substance having a glass transition temperature (Tg) in a range of -20°C to 70°C and the polymer substance having a glass transition temperature (Tg) in a range of -65°C to 10°C is in a range of 70:30 to 30:70.

4. Dust-free paper containing that composition for dust-free paper according to any one of Claims 1 to 3.

5. Dust-free paper according to Claim 4, wherein the composition for dust-free paper is contained an amount of 3wt% to 100wt% by the weight of paper.

6. Dust-free paper according to Claim 4, wherein the composition for dust-free paper is contained in an amount of 5wt% to 50wt% by the weight of paper.

7. A method for producing dust-free paper wherein a polymer composition is prepared by mixing a polymer substance having a glass transition temperature (Tg) in a range of -20°C to 70°C and another polymer substance having a glass transition temperature (Tg) in a range of -65°C to 10°C, a difference between their glass transition temperatures being 30°C or above, and an average glass transition temperature (tg) being in a range of-30°C to 20°C, at a ratio of 95:5 to 5:95 and the produced composition for dust-free paper is carried on paper.